

Novel Ionomers Based on Blends of Ethylene–Acrylic Acid Copolymers with Poly(vinyl amine)

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SYNOPSIS

The polymerization of *N*-vinyl formamide followed by hydrolysis yields a linear, water-soluble poly(vinyl amine). The high concentration of pendant primary amine groups leads to a polymer with an interesting set of properties. Complexation with water-soluble anionic polyelectrolytes in water solutions leads to a highly water-insoluble material. The study described herein investigated the phase behavior/properties of melt blends of poly(vinyl amine) with ethylene–acrylic acid (EAA) copolymers of less than 10 wt % acrylic acid. The calorimetric and dynamic mechanical analyses of the resultant blends show that the vinyl amine groups are accessible to the acrylic acid groups of the copolymers and the major property changes occur up to the stoichiometric addition of vinyl amine/acrylic acid. At higher levels of vinyl amine (vinyl amine/acrylic acid mol ratio > 4), additional poly(vinyl amine) forms a separate phase. The mechanical, dynamic mechanical, and calorimetric properties of these blends below the stoichiometric ratio show analogous trends as with typical alkali/alkaline metal neutralization. These characteristics relative to the base EAA include improved transparency, lower melting and crystallization temperature, lower level of crystallinity, and increased modulus and strength. The emergence of the β transition in dynamic mechanical testing is pronounced with these blends (as with alkali/alkaline metal neutralization), indicative of microphase separation of the amorphous phase into ionic-rich and ionic-depleted regions. A rubbery modulus plateau for the blends exists above the polyethylene melting point, demonstrating ionic crosslinking. Above 150°C exposure, further modulus increases occur presumably due to amide formation. This study demonstrates that the highly polar poly(vinyl amine) can interact with acrylic acid units in an EAA copolymer comprised predominately of polyethylene (>90 wt %). The thermodynamic driving force favoring ionic association overrides the highly unfavorable difference in composition. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

A class of polymers termed ionomers generally refers to the combination of a polymer backbone of low polarity in which ionic groups are dispersed. The ionic groups can aggregate into ionic domains and yield unique properties significantly different from the unmodified polymer backbone. Commercial ionomers include the ethylene–(meth)acrylic acid ionomers which are partially neutralized with Na⁺ or Zn²⁺ cations. The partial neutralization of ethylene–

(meth)acrylic acid copolymers leads to improved transparency, higher modulus and strength, and increased viscosity above the polyethylene melting point.

Microphase separation of ionomers into phases of low and high dielectric constants has been studied experimentally and theoretically. The initial theoretical treatment of clustering of ions in polymers was presented by Eisenberg¹ and remains a prominent reference on this subject. It was shown that ions in polymers (of low dielectric constant) exist as pairs or higher multiplets (up to eight pairs). The ion multiplets can cluster into larger ionic regions. Additional theories of aggre-

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gation in ionomers were reviewed by Mauritz.² Various descriptive models have been proposed based often on the experimental analysis of X-ray scattering data.³⁻⁵

The X-ray scattering data (both small angle and wide angle) on several different polymer systems indicated ionic domains of ~ 20 nm.^{5,6} Otocka and co-workers,^{7,8} however, proposed that a uniform distribution of ionic groups existed in the amorphous phase based on their interpretation of NMR and dynamic mechanical data. A comprehensive review on the proposed models for ionic aggregation in ionomers has been well covered by MacKnight and Earnest.⁹

The dynamic mechanical properties of the ethylene-(meth)acrylic acid copolymers were studied as a function of neutralization in various reports. Longworth and Vaughan³ noted the emergence of a transition in the range of the β transition (-20°C) typical for branched polyethylene. MacKnight et al.¹⁰ also noted an emergence of a β transition with neutralization of similar ethylene/methacrylic acid copolymers. An increase in the magnitude and position of the α relaxation for ethylene/methacrylic acid copolymers was also observed with increasing ionization. The α transition is generally ascribed to the T_g of the copolymer. These data indicate that ionization leads to domain structure (polar ion-rich regions, nonpolar ethylene-rich regions) yielding phase separation. The properties resemble similarities to phase-separated block copolymers. Another important variable involves the reduction in crystallinity with increasing ionization. As the structure in the melt persists, the rearrangement of polyethylene chains to crystallize to their full extent is restricted. With a decrease in crystallinity (and spherulite size) and with domain structure size smaller than the wavelength of light improved transparency results. Similar property changes were noted by Bonotto and Bonner¹¹ with the ionization of ethylene-acrylic acid (EAA) copolymers with monovalent ions (Na^+ , K^+ , Li^+) and divalent ions (Ca^{2+} and Mg^{2+}); a domain structure was also proposed.

It has been recognized that NH_4^+ can also be employed as a monovalent ion for the neutralization of ionomers.¹² Polymeric amines, however, have not been studied to any significant degree. With the emergence of synthetic methods to produce poly(vinyl amine) (PVAm) from poly(*N*-vinyl formamide),^{13,14} a study was undertaken to investigate PVAm's as well as vinyl alcohol/vinyl amine copolymers in blends with

AA-containing polymers—specifically, EAA copolymers.

Ionomer blends were studied by Eisenberg and co-workers¹⁵⁻¹⁷ involving systems such as sulfonated polyisoprene and blends with styrene/4-vinylpyridine copolymers. The potential of ionic bond formation expectedly leads to improved mechanical compatibility at lower levels of ionic groups and miscibility at higher levels. The aggregation of ionic groups in these polymers in which the counterion is attached to another polymer chain will be quite different than the case of alkali and alkaline metal cations. With anionic polymers such as poly(acrylic acid), PVAm forms a very strong polyelectrolyte complex which is only soluble at high or low pH. Polyethyleneimine also develops strong polyelectrolyte complexes, and upon heating, amide formation can result.¹⁸ Many examples of strong polyelectrolyte complexes based on mixtures of anionic and cationic polymers have been noted in the literature.¹⁹ Limited examples exist of highly cationic or anionic polymer mixtures with copolymers containing a low amount of the counterfunctionality such as the study discussed herein.

Thus, the particular system investigated in this study is somewhat unique compared to other ionomer blends. PVAm offers a very high concentration of primary amine groups which can neutralize carboxylic acid groups, if accessible. It will be of interest to determine if the EAA copolymers at high ethylene content will allow for accessibility of the highly polar PVAm.

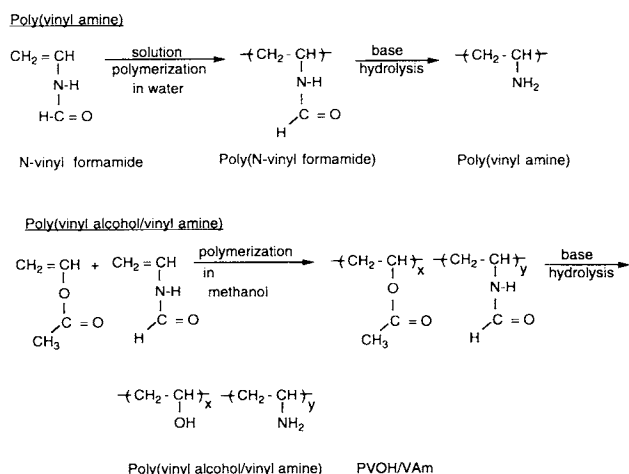
EXPERIMENTAL

The blends chosen for this investigation involved EAA copolymers of 6.5 and 9.0 wt % AA, respectively, Primacor 1320 and 1430 (Dow Chemical Co.). These EAA copolymers are designated as EAA (6.5% AA) and EAA (9% AA) in the following discussions. The PVAm and PVOH/VAm copolymers employed in blends with the noted EAA copolymers in this study are listed in Table I with the pertinent molecular weight and composition data. The PVAm was prepared via the polymerization of *N*-vinyl formamide followed by base hydrolysis. Two PVAm samples were employed in this study (PVAm-1 and PVAm-2). Both had similar M_n values for the precursor poly(*N*-vinyl formamide) and were fully hydrolyzed (>99%). The sodium formate, a reaction byproduct, was removed via dialysis. PVOH/VAm copolymers were prepared via vinyl acetate/*N*-vinyl

Table I Pertinent Data for PVAm and PVOH/VAm Samples Employed in Blends

| | | |
|--------------------------------|---|-----------------------------------|
| <u>PVAm-1</u> | Precursor PNVF > 99% hydrolyzed by NMR (mol %) | $M_w = 72,300$ $M_n = 21,700$ |
| <u>PVAm-2</u> | Precursor PNVF > 99% hydrolyzed by NMR (mol %) | $M_w = 42,300$ $M_n = 21,200$ |
| <u>PVOH/VAm (5 mol % VAm)</u> | Composition by NMR (mol ratio) (VOH/VAm/ <i>N</i> -vinyl formamide) = 94/5/1 | $M_w = 98,900$ $M_n = 61,400$ |
| <u>PVOH/VAm (10 mol % VAm)</u> | Composition of NMR (mol ratio) (VOH/VAm/ <i>N</i> -vinyl formamide) = 89/10/1 | $M_w = 106,000$ $M_n = 67,800$ |

formamide copolymerization followed by base hydrolysis of both vinyl acetate and *N*-vinyl formamide monomer units. The two PVOH copolymers employed in this study contained approximately 5 and 10 mol % VAm and will be noted as PVOH/VAm (5 mol % VAm) and PVOH/VAm (10 mol % VAm). The generalized synthesis procedure for PVAm and PVOH/VAm is shown below:



Blends of the EAA copolymers with PVAm and PVOH/VAm copolymers were prepared in a Brabender melt mixer at temperatures slightly above the melting point of the EAA copolymers (>100°C). To facilitate the mixing, PVAm and PVOH/VAm were added with water incorporation (0–30% water for PVAm and 30–50% water for PVOH/VAm). PVAm exhibits a T_g of 42°C (dry) and is amorphous; thus, water addition is not necessary. PVOH/VAm exhibits a T_g of 84°C (5% VAm) and 99°C (10% VAm) but has residual PVOH crystallinity; thus, water incorporation was necessary. Water devolatilization occurred during mixing. The resultant mixtures were compression molded at 120–140°C for test specimens for dynamic mechanical, me-

chanical property, and calorimetry measurements. The compression molding temperature and time were minimized to keep amide formation low.

The dynamic mechanical testing was conducted on specimens (dry and saturated with water) utilizing a Rheometrics RSA-II in the tensile mode (6.28 rad/s). Sample thicknesses ranged from 20 to 35 mil. The mechanical properties (stress-strain) were determined on die-cut tensile specimens employing an Instron testing apparatus (Model 1101). Calorimetry measurements were conducted utilizing a Perkin-Elmer DSC-7 differential scanning calorimeter.

RESULTS AND DISCUSSION

The blends involving PVAm (PVAm-1) and Primacor 1320 EAA (6.5% AA) subjected to dynamic mechanical testing yield results illustrated in Figures 1 and 2. The mechanical loss data ($\tan \delta$) (Fig. 1) show a broad transition with a peak at 40°C attributed to the glass transition of EAA (6.5% AA). A shoulder in this transition (–10°C) is believed to be the β transition typical of branched low-density polyethylene.²⁰ The γ transition (–130°C) is typical for ethylene-based polymers comprising $-\text{CH}_2-$ _{*n*} units of $n \geq 4$ attributed to a crankshaft rotation transition. With the addition of 10 wt % PVAm, the T_g increases (to 65°C) and the β transition emerges as a significant transition. With 20 wt % PVAm, the T_g and β transition remain; however, a transition emerges at 20°C believed to be phase-separated PVAm which emerges as a much larger peak for the 50/50 blend. As the T_g of PVAm (dry) is 42°C, it appears that residual water from the mixing procedure was not adequately removed. This was corrected in the next series of experiments where water was not added to facilitate the mixing. The tensile modulus-temperature data reflects the transition

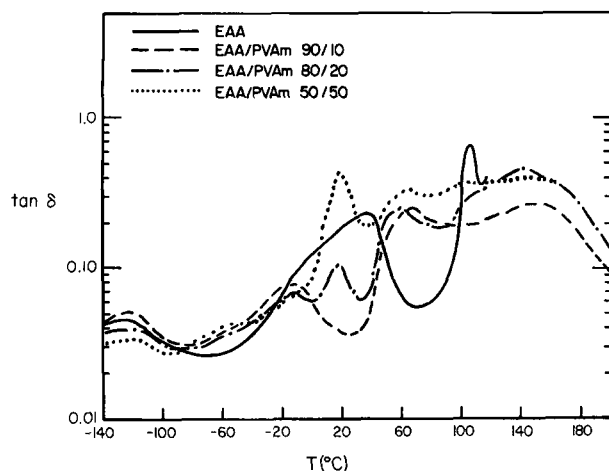


Figure 1 Mechanical loss-temperature data for EAA (6.5 wt % AA) copolymer blends with PVAm (PVAm-1).

changes occurring in EAA (6.5% AA) with PVAm addition. It is of interest to note that a rubbery modulus plateau occurs above the polyethylene melting point, indicative of ionic crosslinking as would be expected if PVAm is accessible to the AA units of EAA.

The dynamic mechanical properties of PVAm (dry) and with 14% water sorption are illustrated in Figure 3 for reference purposes. PVAm is amorphous, with a T_g of 42°C. The water sorption (conducted at low relative humidity) was determined from a TGA weight loss experiment. The Fox equation²¹ relating T_g of plasticized mixtures,

$$\frac{1}{T_g} = \frac{W_a}{T_{g_a}} + \frac{W_b}{T_{g_b}}$$

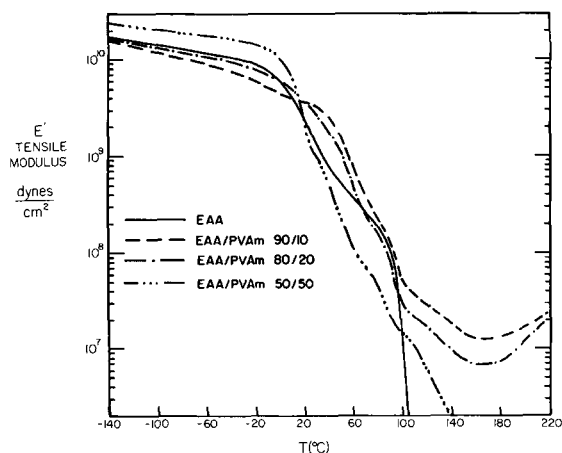


Figure 2 Tensile modulus-temperature data for EAA (6.5 wt % AA) copolymer blends with PVAm (PVAm-1).

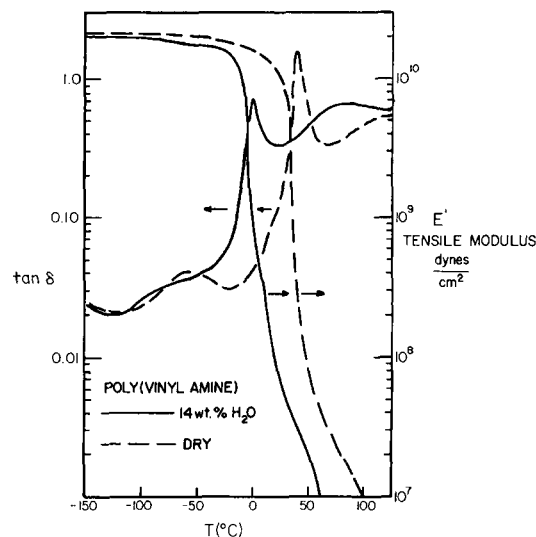


Figure 3 Dynamic mechanical properties for PVAm (PVAm-2) (dry and with 14 wt % water).

can be employed to predict the T_g of a 14 wt % H₂O plasticized PVAm. The T_g of amorphous water has been previously determined²² to be -136°C. The predicted value of -6°C agrees with the experimental value of -3°C. The next series of experiments involved EAA (9% AA). The PVAm employed in these blends was PVAm-2. The mechanical loss (tan δ) vs. temperature results are shown in Figures 4 and 6 for various EAA (9% AA)/PVAm combinations. EAA (9% AA) does not exhibit a shoulder in the range of the β transition. The addition of PVAm (5, 10, and 20 wt %) yields a clearly resolvable β transition and a significant increase in T_g . At 40 and 60 wt % PVAm, the transition for PVAm ap-

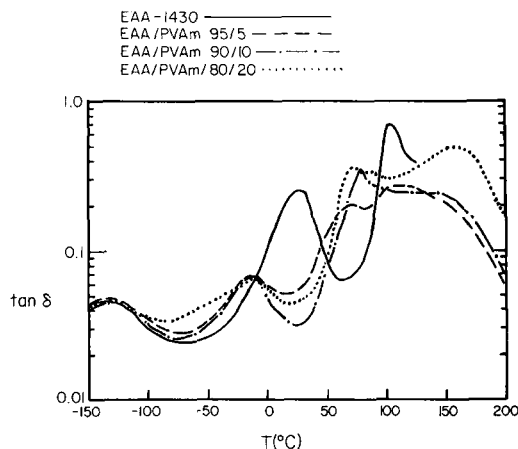


Figure 4 Mechanical loss-temperature data for EAA (9 wt % AA) copolymer blends with PVAm (PVAm-2).

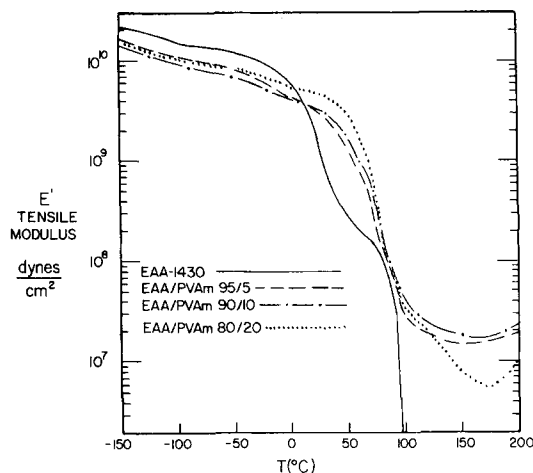


Figure 5 Tensile modulus-temperature data for EAA (9 wt % AA) copolymer blends with PVAm (PVAm-2).

pears, indicating phase separation presumably due to full neutralization of the acrylic acid units leaving residual PVAm. The tensile modulus-temperature data (Figs. 5 and 6) show the modulus-plateau above melting point of polyethylene with the highest plateau at 5 and 10 wt % PVAm, indicative of ionic crosslinking. An increase in modulus above 150°C is presumably due to amide formation.

The blends of EAA (9% AA) with 10 and 20 wt % PVOH/PVAm (10 mol % VAm) exhibited homogeneous blends with transparency improved over the control EAA (9% AA). The mechanical loss data (Fig. 7) show an increase in the T_g of EAA (9% AA) with a hint of a shoulder in the range of the β transition at 20 wt % PVOH/VAm addition.

The mechanical properties for the EAA (9% AA) blends with PVOH/VAm and PVAm are listed in Table II. A significant increase in tensile modulus occurs with the addition of PVAm even at very low levels. Increased tensile strength and lower elongation at break also result with PVAm addition. The resultant blends exhibit "leather"-like properties similar to conventional ethylene-(meth)acrylic acid ionomers.²³ Similar results are observed with the addition of PVOH/VAm to EAA. It is of interest to note that EAA (9% AA) with 20 wt % PVOH yields poorer properties than do the PVOH/VAm blends. The stress-strain curves on these blends (Figs. 8 and 9) demonstrate the improved properties of PVAm or PVOH/VAm addition to EAA. The comparison of PVOH with PVOH/VAm in Figure 9 clearly demonstrates the improved mechanical compatibility via introduction of ionically interacting units.

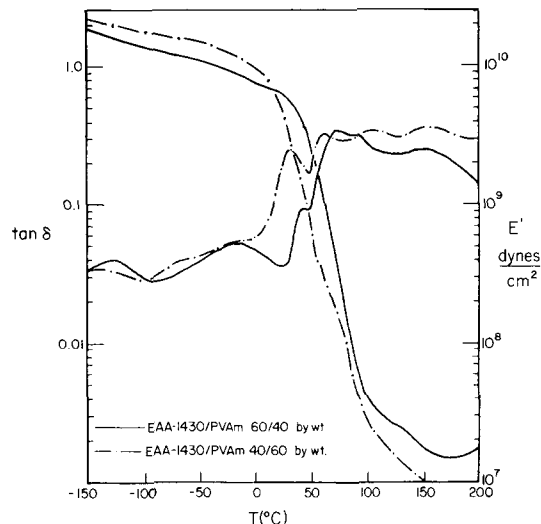


Figure 6 Dynamic mechanical property data for EAA (9 wt % AA) copolymer blends with PVAm (PVAm-2).

The addition of PVAm and PVOH/VAm to the EAA copolymers led to miscibility at lower levels of addition, yielding mechanical compatibility. The phase intermixing would suggest changes in the crystallinity and crystallization kinetics for the polyethylene segments of the EAA copolymers. Calorimetry results were obtained on the compression-molded specimens, with results listed in Table III. A significant melting point depression, decreasing peak temperature of crystallization (T_c), and heat of crystallization/heat of fusion results. In several cases, the first heating gave bimodal melting curves which were not reproduced in the second heating cycle. The decreasing melting point, level of crys-

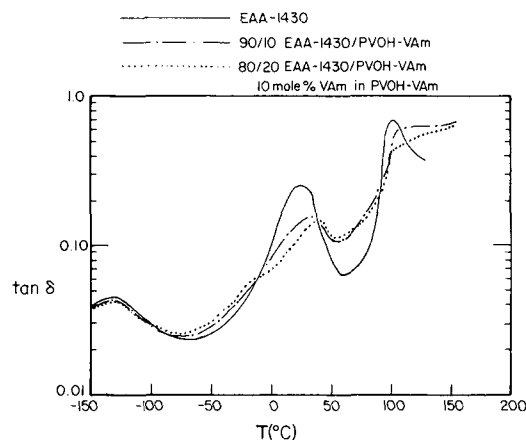


Figure 7 Mechanical loss data for EAA (9 wt % AA) blends with VAm copolymers (PVOH/VAm: 10 mol % VAm).

tallinity, and slower crystallization rate are attributed to the structure existing in the melt which prevents polyethylene chains from freely accessing the growing crystalline structure. This is similar to peroxide or radiation crosslinking polyethylene in the melt.

The blends comprising EAA (9% AA) and PVAm or PVOH/VAm were utilized for water-sorption and extraction determination. The samples were predried and then immersed in distilled water until equilibrium was reached and then dried to a constant weight. The water sorption (based on final dry weight) and extractables (based on initial dry weight) were determined as noted in Table IV. A sample of PVOH (Airvol 205) was included for comparison. It is interesting to note that up to 20 wt % PVAm or PVOH/VAm in blends with EAA (9% AA) virtually no extraction is observed, thus agreeing with the dynamic mechanical data as well as the calorimetry data. The PVOH comparison with PVOH/VAm shows a significant difference. Although PVOH as a minor constituent is trapped as a discontinuous phase, the extractable level is significantly higher than for PVOH/VAm. The dynamic mechanical properties of a water-immersed sample of EAA (9% AA)/PVAm (80/20 by wt) are illustrated in Figure 10 compared with the dry sample data. The T_g of the ionic-rich phase loses resolution, possibly due to varying degrees of hydration and/or clustering of the ionic domains. The much

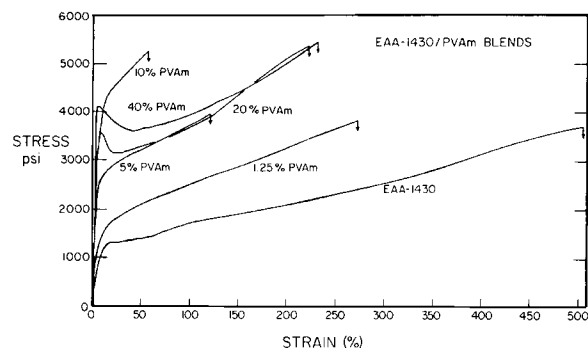


Figure 8 Stress-strain data for EAA copolymer (9 wt % AA) blends with PVAm (PVAm-2).

lower modulus of the water-immersed sample in the temperature range of -25 to 75°C reflects the plasticization of the ionic domains by water.

It is apparent from the macroscale data that the major changes in properties occur at addition levels less than 10 wt % PVAm to EAA (9% AA). If every AA group were accessible to every VAm group, then full neutralization will occur at 5 wt % PVAm addition to EAA (9% AA). This is well illustrated in Figure 11, where the heat of fusion, the heat of crystallization, melting point, crystallization temperature, and tensile modulus are compared as a function of PVAm content in the blend. These data all indicate that the neutralization of the AA units occurs in the range of 5–10 wt % PVA. The level of acces-

Table II Mechanical Property Data EAA (9% AA)/PVAm and EAA (9% AA)/PVOH/VAm Blends

| | Tensile Modulus (psi) | Tensile Strength (psi) | % Elongation |
|----------------------|--------------------------|---------------------------|--------------|
| EAA (9% AA)/PVAm | | | |
| 100/0 | 16,740 | 3685 | 507 |
| 98.75/1.25 | 20,230 | 3910 | 273 |
| 97.5/2.5 | 40,670 | 3335 | 101 |
| 95/5 | 52,400 | 3990 | 121 |
| 90/10 | 64,260 | 5265 | 58 |
| 80/20 | 78,340 | 5340 | 224 |
| 60/40 | 88,575 | 5420 | 236 |
| 40/60 | 77,970 | 5500 | 207 |
| 0/100 | 125,800 | 5050 | 83 |
| EAA (9% AA)/PVOH/VAm | | | |
| 90/10 (5 mol % VAm) | 29,680 | 3030 | 124 |
| 80/20 (5 mol % VAm) | 57,150 | 3720 | 107 |
| 90/10 (10 mol % VAm) | 42,800 | 3600 | 233 |
| 80/20 (10 mol % VAm) | 64,170 | 3430 | 73 |
| EAA (9% AA)/PVOH | | | |
| 80/20 (Airvol 205) | 24,590 | 1790 | 148 |

Properties were measured dry. Tensile strength was measured as maximum stress on stress-strain curve.

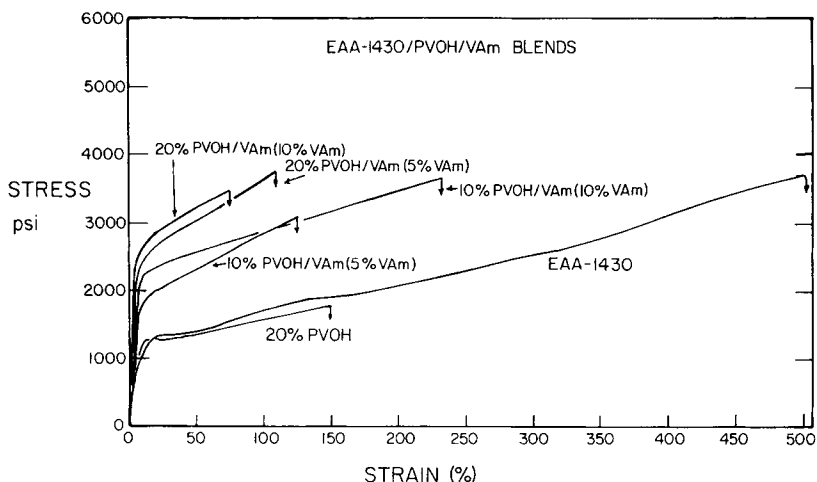


Figure 9 Stress-strain data for EAA copolymers (9 wt % AA) blends with PVOH/VAm copolymers. (PVOH/VAm: 5 mol % and 10 mol % VAm).

sibility of VAm to the AA units thus appears to be quite good. Significant phase separation (separate PVAm phase) occurs at > 20 wt % PVAm. This would indicate that PVAm chains are only partially neutralized prior to phase separation. In essence, addition of PVAm above the stoichiometric VAm/AA level yields lower levels of VAm neutralization until phase separation of PVAm occurs. As the AA units are essentially neutralized, further changes in the properties are modest. Although not within the scope of this investigation, this could be resolved by spectroscopic investigations.

The dynamic mechanical and calorimetric results show that PVAm and PVOH/VAm copolymers are

able to ionically associate with AA units in EAA copolymers. The maximum level of association qualitatively appears to occur at equimolar levels of AA and VAm. At higher levels of VAm, phase separation of PVAm occurs, yielding a blend comprising a phase of crystalline polyethylene, amorphous EAA domains neutralized with PVAm, and PVAm-rich phases presumably containing limited concentrations of the EAA copolymer. It is interesting to note that PVAm as well as VAm copolymers are able to ionically bond with AA units in a copolymer primarily composed of ethylene units. The thermodynamically favorable ionic interaction overrides the unfavorable nonpolar, hydrophobic predominance of ethylene units in the EAA copolymer.

The key to the analysis of the phase behavior of the subject blends resides in the emergence of the β transition. The β transition of branched polyethylene generally appears as a shoulder in the $\tan \delta$ data. This is also observed in ethylene copolymers at lower levels of comonomer content [compare EAA (6.5% AA) vs. EAA (9% AA)]. Specifically, a shoulder exists for the lower AA copolymer EAA (6.5% AA), but disappears for EAA (9% AA). With the addition of PVAm, the β transition strongly reappears as a distinct transition. This implies that domain formation is occurring with neutralization of the AA units, namely, ethylene-rich domains in the amorphous state and ionic domains rich in AA-VAm ionic complexes similar to that observed with alkali/alkaline metal neutralization of (meth)acrylic acid containing copolymers.

The decrease in melting point, heat of fusion, heat of crystallization, and decrease in the temperature of maximum crystallization rate (T_c) of polyethylene

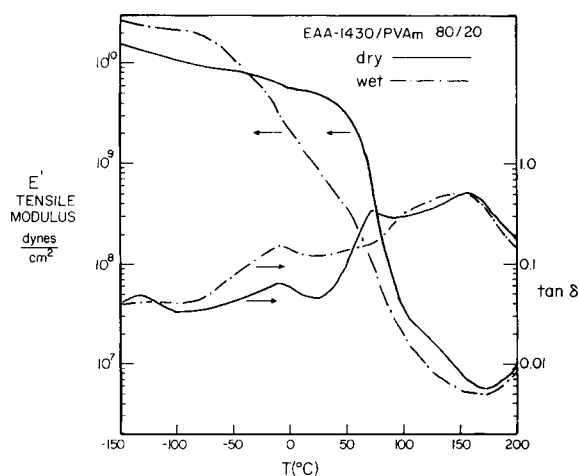


Figure 10 Dynamic mechanical properties of an EAA copolymer (9 wt % AA) blend with PVAm (PVAm-2) (80/20 by wt) (dry vs. equilibrated in water).

Table III Calorimetry Results on EAA (9% AA)/PVAm Blends

| EAA (9% AA)/PVAm Wt. Ratio | First Scan (Heating) | | First Scan (Cooling) | | Second Scan (Heating) | |
|-------------------------------|----------------------|-----------------------|-------------------------|-----------------------|--------------------------|-----------------------|
| | T_m (°C) | ΔH_f (J/g) | T_m (°C) | ΔH_c (J/g) | T_m (°C) | ΔH_f (J/g) |
| 100/0 | 95.8 | 63.4 | 75.2 | 78.5 | 95.6 | 72.1 |
| 97.5/2.5 | 91.1 | 54.6 | 68.6 | 61.4 | 92.5 | 65.5 |
| 95/5 | 73.5, 90.5 | 44.5 | 52.4 | 38.1 | 89.5 | 31.5 |
| 90/10 | 79.5 | 33.3 | 45.7 | 20.2 | 89.4 | 17.4 |
| 80/20 | 49.5, 87.0 | 37.2 | 47.8 | 12.8 | 85.9 | 19.8 |
| 60/40 | 81.6 | 39.5 | 47.6 | 12.8 | 85.3 | 15.3 |

Samples were measured dry. The first scan started at -20°C with a heating rate of $10^\circ\text{C}/\text{min}$ up to 150°C . At 150°C , the temperature direction was reversed with a cooling rate of $10^\circ\text{C}/\text{min}$ down to -20°C . The sample was then heated again at $10^\circ\text{C}/\text{min}$ to 150°C .

with increasing PVAm content is the resultant effect of ionic association in the melt which restricts the diffusion of ethylene-rich units to the growing crystalline structure. At PVAm contents above the stoichiometric ratio of VAm/AA, the effect on the crystallization characteristics is virtually eliminated due to the development of PVAm phase structures.

The amount of amide formation remains unresolved at this stage of the investigation. However, it appears from the modulus-temperature data that amide formation is occurring with temperature exposure above 150°C . Spectroscopic measurements that could resolve this issue also, however, were not within the scope of this investigation.

CONCLUSIONS

The addition of PVAm to EAA copolymers (6.5–9.0 wt % AA) leads to major property changes at low

levels of addition up to the stoichiometric ratio of VAm/AA. These property changes include increased modulus and tensile strength, decreased elongation, and improved transparency, very similar to that noted for alkali/alkaline metal neutralization of similar copolymers. Additionally, major changes in the degree of crystallinity, the melting point, and the crystallization temperature also occur. Above the stoichiometric ratio of VAm/AA, the property changes are much lower with continued PVAm addition. Phase separation yielding PVAm regions occurs above a VAm/AA molar ratio of 3–4. The modulus-plateau above the T_g indicates ionic crosslinking. Increasing the temperature above 150°C during dynamic mechanical testing shows an additional modulus increase, presumably due to covalent (amide) bond formation. The β transition typical for branched polyethylene prominently appears (-20°C) with PVAm addition to the EAA copolymers, showing evidence of microphase separation

Table IV Water Sorption and Extraction Data

| Sample Description | % Water Sorption | % Extractables |
|--------------------------------------|------------------|----------------|
| 60/40 PVAm/EAA (9% AA) | 365.6 | 22.6 |
| 40/60 PVAm/EAA (9% AA) | 88.4 | 1.44 |
| 20/80 PVAm/EAA (9% AA) | 25.1 | < 0.1 |
| 10/90 PVAm/EAA (9% AA) | 2.78 | < 0.1 |
| 5/95 PVAm/EAA (9% AA) | 1.48 | < 0.1 |
| 2.5/97.5 PVAm/EAA (9% AA) | 0.904 | < 0.1 |
| 20/80 PVOH/VAm (10% VAm)/EAA (9% AA) | 2.43 | < 0.1 |
| 20/80 PVOH/VAm (5% VAm)/EAA (9% AA) | 2.22 | < 0.1 |
| 20/80 PVOH/EAA (9% AA) | 2.41 | 0.86 |
| EAA (9% AA) | 0.184 | < 0.1 |

Measured on compression-molded samples after storage in a desiccator. % water sorption measured after equilibrium was reached in water immersion. % extractables determined after drying to constant weight.

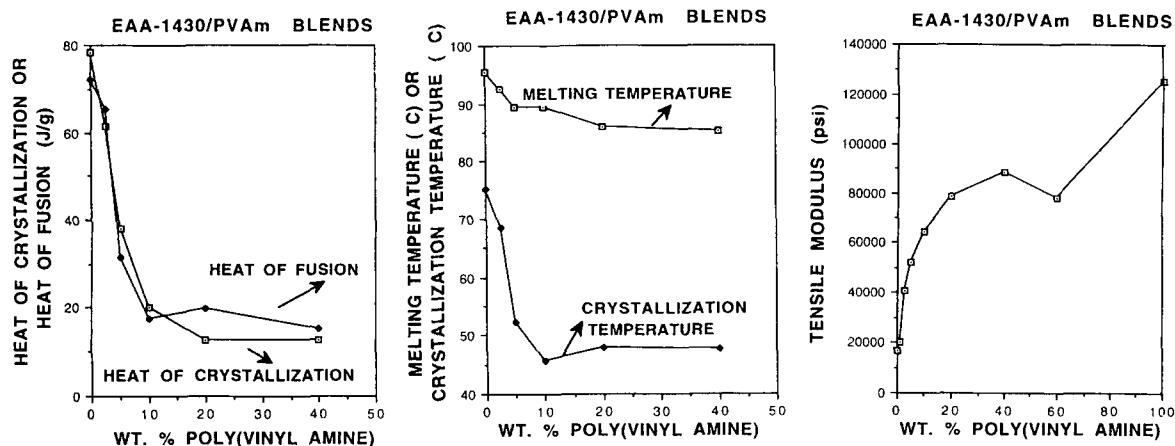


Figure 11 Comparison of heat of fusion, heat of crystallization, melting point, crystallization temperature, and tensile modulus of EAA copolymer (9 wt % AA) as a function of PVAm (PVAm-2) addition.

into ionic-rich domains and nonionic (polyethylene) domains. This is also characteristic of alkali/alkaline metal neutralization of similar ethylene copolymers.

It is interesting to note that the highly polar PVAm can interact at the molecular scale with the polyethylene containing low amounts of AA units. The thermodynamic driving force for ionic association overrides the highly unfavorable compositional differences.

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Received September 25, 1995

Accepted January 14, 1996